

Field, Laboratory and Model Studies of CDOM

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LONG-TERM GOALS

The principal long-term objective of this work is to determine what factors control the distribution and dynamics of the chromophore-containing constituents of dissolved organic matter (CDOM) in marine and estuarine waters. Two important secondary objectives are 1) to elucidate the photochemical properties of the CDOM and how photochemical reactions affect the optical properties and secondary reactivity of the CDOM, 2) to obtain a clearer understanding of the nature of the underlying light-absorbing constituents that produce the absorption spectrum of the CDOM. Field measurements are employed to determine the distribution of CDOM and its impact on the aquatic light field, whereas a combination of field and laboratory experiments are used to test mechanisms of its formation and loss. Model systems and spectroscopic methods are being employed to probe the nature of the constituents giving rise to the observed absorption spectrum of CDOM.

OBJECTIVES

Over the last year, our principal near-term objectives were as follows:

1. Complete one final field expedition (March 2003) and submit the results of our seasonal study for publication (special edition of *Marine Chemistry*).
2. Organize and co-chair with Richard Zepp an American Chemical Society Symposium on "Impact of Photochemical Processes in the Hydrosphere."
3. Acquire and analyze data from a set of laser photobleaching experiments and initiate a new set of experiments in collaboration with Drs. Elizabeth Kujawinski and Rossana Del Vecchio to examine the structural changes within CDOM resulting from wavelength selective photodegradation, using a very high resolution mass spectrometer (FT-ICR).
4. Complete a number of photochemical studies initiated under prior ONR-supported work (Photochemical Sinks of Organic Pollutants in Estuarine and Near-Shore Environments).

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14. ABSTRACT The principal long-term objective of this work is to determine what factors control the distribution and dynamics of the chromophore-containing constituents of dissolved organic matter (CDOM) in marine and estuarine waters. Two important secondary objectives are 1) to elucidate the photochemical properties of the CDOM and how photochemical reactions affect the optical properties and secondary reactivity of the CDOM, 2) to obtain a clearer understanding of the nature of the underlying light-absorbing constituents that produce the absorption spectrum of the CDOM. Field measurements are employed to determine the distribution of CDOM and its impact on the aquatic light field, whereas a combination of field and laboratory experiments are used to test mechanisms of its formation and loss. Model systems and spectroscopic methods are being employed to probe the nature of the constituents giving rise to the observed absorption spectrum of CDOM.				
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APPROACH

Over the past six years, we have carried out a systematic series of field studies examining the distribution of CDOM in the Middle Atlantic Bight (MAB) and the Delaware and Chesapeake Bays over Spring and Summer and into early Fall. The objectives of these studies were 1) to determine the spatial and seasonal contribution of CDOM absorption to the total light absorption in the UV and visible spectral ranges, 2) to infer sources and sinks of CDOM based on changes in its spatial and temporal distributions, and 3) to examine the effects of water-column stratification on the distribution and magnitude of CDOM absorption on the shelf of the MAB over the summertime. The results and conclusions of these studies, which are detailed in Del Vecchio (2002) and a submitted manuscript (Del Vecchio and Blough, 2003), are summarized below.

Both field and laboratory studies have been used to investigate the sources and sinks of CDOM in the marine environment. For example, field measurements first indicated that photochemistry could act as a significant sink of CDOM in stratified surface waters over the summer (Vodacek et al., 1997), with more recent studies providing very strong support for these conclusions (Del Vecchio and Blough, 2003). Laboratory photobleaching studies have been employed to test whether the time scale of this process and the changes in CDOM spectral shape are compatible with the field observations (Del Vecchio and Blough, 2002). Further, models for the photobleaching of CDOM have been developed from this detailed data set (Del Vecchio and Blough, 2002; Goldstone et al., to be submitted).

Because we know almost nothing about the structural nature of the underlying chromophores giving rise to the rather unique absorption spectrum of the CDOM, we have initiated a series of laboratory studies aimed at addressing this issue. Techniques that we are employing include laser photobleaching experiments of CDOM in high viscosity solvents, the analysis of the absorption spectra of mixtures of small molecules in solution, high-resolution mass spectrometry and photochemical studies of compounds thought to be constituents of CDOM (e.g., quinones; Pochon et al., 2002).

WORK COMPLETED

1. A final field expedition was undertaken in March 2003, the results of which were incorporated in our long-term seasonal study. The results from this seasonal study were submitted for publication in the special issue on CDOM in *Marine Chemistry*; the abstract of this paper is provided below in **Results**.
2. In 2003, co-organized and co-chaired with Richard Zepp a major ACS symposium (34 papers) entitled "Impact of Photochemical Processes in the Hydrosphere", and was editor of a special issue of *Aquatic Sciences* that resulted from this symposium (10 papers). This special issue will be published in December 2003.
3. A complete set of laser photobleaching experiments at wavelengths covering the visible and ultraviolet wavelengths has been collected and analyzed, with a manuscript on this topic currently being developed. In addition, E. Kujawinski, R. Del Vecchio and I have initiated studies of the structural changes that occur within CDOM upon photobleaching at selected wavelengths or wavelength regimes employing an FT-ICR (Fourier Transform-Ion Cyclotron Resonance) mass spectrometry at the National High Magnetic Field Laboratory.
4. Completed our work on the mechanisms of the photodegradation of polycyclic aromatic hydrocarbons that was initiated with prior ONR support. The results of this work have been submitted for publication (Fasnacht and Blough, 2003a,b; abstracts provided below). The work

for a second paper on the photochemistry of 1,4-benzoquinones in aqueous solution has been completed and a manuscript is in preparation (Gan et al., 2004).

RESULTS

Spatial and seasonal distributions of CDOM absorption, fluorescence (excited at 355 nm) (F_n) and dissolved organic carbon (DOC) concentration in coastal waters of the Middle Atlantic Bight (MAB) were acquired. A linear relationship was observed between CDOM absorption at 355 nm ($a_{\text{CDOM}}(355)$) and F_n on the shelf of the MAB ($a_{\text{CDOM}}(355) \leq 1 \text{ m}^{-1}$), but this relationship curved downward for higher $a_{\text{CDOM}}(355)$ and F_n values in the Chesapeake and Delaware Bay source waters ($a_{\text{CDOM}}(355) \geq 1 \text{ m}^{-1}$), suggesting the presence of different end-members with higher $F_n/a_{\text{CDOM}}(355)$ ratios, the occurrence of a photochemical/biological processing of the CDOM as it moves down the estuaries or the involvement of both of these processes. Strong evidence was acquired for the photobleaching of CDOM in the surface waters of the MAB during summertime stratification, as indicated by the highly non-linear dependence of $a_{\text{CDOM}}(355)$ and F_n on salinity in surface waters, the concomitant increase of the CDOM spectral slope parameter (S) and the much lower ratio of a_{CDOM} to DOC ($a_{\text{CDOM}}/\text{DOC}$) observed in surface waters. The $a_{\text{CDOM}}/\text{DOC}$ ratio decreased by over an order of magnitude with increasing salinity, owing primarily to two reasons: 1) the substantial photobleaching of CDOM in the surface waters of the shelf and 2) the very different content of CDOM and DOC in the fresh water and oceanic end-members. These results indicate that CDOM represents only a small portion of the DOC pool in off shore waters, and that the sources and sinks of CDOM and DOC are uncoupled despite the often-observed correlation between CDOM and DOC in the coastal environment (Del Vecchio and Blough, 2003; see also Blough and Del Vecchio, 2002).

An analysis of the monochromatic bleaching kinetics first indicated to us that a model based on a simple superposition of numerous chromophores undergoing photobleaching independently could not apply (Del Vecchio and Blough, 2002). This conclusion further implies that the absorption spectrum of CDOM cannot arise solely from a simple superposition of the spectra of numerous independent chromophores. Instead, these results suggest that there must be electronic coupling between chromophores. To further test this possibility, a series of ‘hole-burning’ experiments were conducted to study the nature of the species that produces the absorption spectrum of humic substances and CDOM (Del Vecchio and Blough, in preparation). A high intensity Nd-YAG laser or a Nd-YAG laser pumping a dye laser was employed to destroy selectively species absorbing at specific wavelengths across the UV and visible wavelengths, with the time course of the absorption losses followed across the entire UV/visible spectrum. To suppress or eliminate the possible effect of reactive oxygen species and secondary photochemistry on the photodegradation, samples were prepared in a high viscosity solvent (90% glycerol/water). The results of these experiments, although too extensive to describe here, show unequivocally that the absorption spectrum of humic substances cannot be explained as a simple sum of the absorption spectra of numerous **independent** chromophores (Del Vecchio, 2002; Del Vecchio and Blough, in preparation). This conclusion is being tested further by the use of wavelength selective photobleaching and high-resolution mass spectrometry.

Our work on PAH photodegradation can be summarized as follows (Fasnacht, 2003; Fasnacht and Blough, 2003a,b): The role of O_2 and photoionization, as well as the involvement of polycyclic aromatic hydrocarbon (PAH) cation radicals (P^+) in the photodegradation of nine PAHs was examined. Photodegradation quantum yields for all PAHs increased with increasing O_2 concentration, illustrating the key role of O_2 in the photodegradation mechanism. In the presence of a series of electron donors (to P^+), the photodegradation rate constants of most PAHs were largely unaffected at low O_2

concentrations ($\leq 250 \mu\text{M}$), indicating that P^+ is not extensively produced. However, at higher O_2 concentrations (up to 1.2 mM), the presence of the donors substantially lowered photodegradation rates for most PAHs, indicating that P^+ is produced and is arising from O_2 reaction with the excited singlet state. Because little P^+ was detected at low O_2 concentrations, and further, because degradation rates were not enhanced in the presence of N_2O , we conclude that photoionization is unimportant. With some exceptions, photodegradation can proceed through reaction of O_2 with both excited singlet and triplet states of the PAHs. Our results indicate that photodegradation via the excited singlet state occurs primarily through electron transfer to O_2 , whereas degradation via the triplet occurs predominately through a direct reaction of O_2 with the PAH within the collision complex (Fasnacht and Blough, 2003a).

The mechanisms by which polycyclic aromatic hydrocarbons (PAHs) photodegrade in dilute ($\leq 25 \text{ nM}$) aqueous solutions under varying O_2 concentrations were examined. Employing previously measured photodegradation quantum yields (acquired in the absence and presence of electron donors to the PAH cation radicals, P^+), excited singlet state ($^1\text{P}^*$) lifetimes, $^1\text{P}^*/\text{O}_2$ quenching rate constants and other parameters from the literature, a kinetic model was developed to analyze the fraction of PAH photodegradation that proceeds via the $^1\text{P}^*$ or excited triplet state ($^3\text{P}^*$), as well as to determine the relative contribution of electron transfer to O_2 versus the direct reaction with O_2 from each state. The analysis supports the following conclusions: 1) $^1\text{P}^*$ is more reactive with O_2 than $^3\text{P}^*$; 2) reaction via $^1\text{P}^*$ proceeds predominantly through electron transfer to produce the P^+ intermediate, whereas reaction via $^3\text{P}^*$ proceeds primarily through direct reaction with O_2 within the collision complex, consistent with the thermodynamic driving forces for electron transfer from these states; 3) although $^3\text{P}^*$ is involved significantly in the degradation of many PAHs, such as anthracene, 9-methylantracene, acenaphthene, and perylene, it is not involved in the degradation of others such as pyrene and benzo[a]pyrene. Under aerobic conditions, photodegradation is likely to be controlled largely by $^1\text{P}^*$ lifetime and reactivity (Fasnacht and Blough, 2003b).

IMPACT APPLICATIONS

Because CDOM contributes significantly to the absorption of coastal and offshore waters, its presence substantially impacts underwater visibility and the aquatic light field. Thus an understanding of its sources and sinks, as well as the nature of the light-absorbing constituents contributing to its spectrum, are needed to predict its spatial and temporal variability in coastal (and open-ocean) waters.

TRANSITIONS

Data that we have collected in the Middle Atlantic Bight continues to be used to validate ocean color algorithms (e.g., Chomko et al., 2003).

RELATED PROJECTS

In other ONR-supported work that finished last year, we examined mechanistic aspects of the photochemistry of CDOM and how photochemistry affects the degradation of organic pollutants. This work entails the detection and quantification of reactive intermediates produced photochemically from the CDOM and their reactions with anthropogenic compounds, principally polycyclic aromatic hydrocarbons and halogenated organic compounds, in an effort to develop predictive models for the

photochemical degradation of these materials. The direct photochemistry of these common pollutants was also examined. Some of this work was completed under this project and is described above.

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HONORS/AWARDS/PRIZES

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| Neil V. Blough | 1999 Research Award, College of Life Sciences, University of Maryland
Editorial Board Member, <i>Aquatic Sciences</i> , (2001-present) |
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